cm^{-1} band is quite well resolved from the $\sim$1400-cm^{-1} envelope and it is possible to measure its depolarization ratio more accurately than for the 1490-cm^{-1} band. However, since it is not possible accurately to measure the depolarization ratio of the 1490-cm^{-1} band, it is not possible completely to rule out the possibility of bidentate nitrate group bonding.

[15] H. Brintzinger and R. E. Hester, *Inorg. Chem.*, **5**, 980 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY,
WALTHAM, MASSACHUSETTS 02154

Kinetics of Oxidation of Some Hydroxylamines by Silver(II)[1]

BY DAN S. HONIG, KENNETH KUSTIN,* AND JOSEPH F. MARTIN

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The kinetics and stoichiometry of the oxidation of hydroxylamine and *O*-methylhydroxylamine by silver(II) have been determined in acid perchlorate media (1.03 $M < [HClO_4] < 5.83\ M$) at 22°. The kinetics of the reaction with *N*-methylhydroxylamine, but not the stoichiometry, has also been determined. In the presence of excess silver(II), stoichiometric measurements indicated that the product of reaction with NH_3OH^+ is NO_3^-; with $NH_3OCH_3^+$ the products are NO_3^- and CO_2, the latter directly detected in stoichiometric amounts by gas chromatographic analysis. No dependence of rate on [Ag(I)] or ionic strength was observed, within experimental error, for hydroxylamine; for *O*-methylhydroxylamine, the rate was inversely dependent on acidity and ionic strength. The acidity variation for both hydroxylamines has been ascribed to the difference in reactivity of Ag^{2+} and $AgOH^+$, which coexist in rapid equilibrium at these hydrogen ion concentrations. For $K_H = [AgOH^+][H^+]/[Ag^{2+}]$, graphical analysis of the rate data at ionic strength 5.95 M yields $K_H = (0.32 \pm 0.14)$ M. With the primed rate constant designating reaction with $AgOH^+$, the rate constants are: for NH_3OH^+, $k < 10^4\ M^{-1}\ sec^{-1}$ and $k' = (1.4 \pm 0.5) \times 10^6\ M^{-1}\ sec^{-1}$; for $NH_3OCH_3^+$, $k < 10^3\ M^{-1}\ sec^{-1}$ and $k' \simeq (2 \pm 1) \times 10^4\ M^{-1}\ sec^{-1}$. For $CH_3NH_2OH^+$, the apparent second-order rate constant, k_{app}, determined by the stopped-flow technique is $k_{app} = (1.6 \pm 0.6) \times 10^5\ M^{-1}\ sec^{-1}$. The mechanisms of these reactions are discussed in terms of free-radical intermediates. Comparison is made with analogous results for oxidation of hydroxylamines by Mn(III), for which the comparable rate constants are approximately one order of magnitude less (NH_3OH^+), and as much as three orders of magnitude less ($NH_3OCH_3^+$). In this and other studies the stoichiometric consumption ratio may vary with the ratio of initial moles of reactants present. An explanation is provided for this behavior in terms of competitive intermediate steps.

Silver(II) is generally an extremely strong, rapidly reacting oxidizing agent in perchlorate media. In fact, for a given substrate, a comparison of its reactivity with that of manganese(III) shows silver(II) to be at least one order of magnitude more rapidly oxidizing than even this highly reactive species.[2,3] The high oxidation potential (~ -2 V)[4] of silver(II) also causes most of its reactions to be irreversible. Consequently, the only fast reaction method available for kinetic measurement is rapid mixing, which has been used in this study.

Reactions of silver(II) with some substrates were too fast to be studied definitively by this method. Its reaction with hydrogen peroxide, hydroquinone, and nitrous acid were found to be essentially complete within the resolution time (2–5 msec, depending on experimental conditions) of our stopped-flow apparatus. *O*-Methylhydroxylamine, present as $NH_3OCH_3^+$ at high acid concentration,[5] was found to have one of the slowest rates of reaction with Mn(III) of the substrates studied.[3a,6] Its rate of reaction with Ag(II) is found to be well within detectable range, suggesting other, more reactive, substrates could also be studied. Hydroxylamine and *N*-methylhydroxylamine, present as NH_3OH^+ and $CH_3NH_2OH^+$, respectively, at high acid concentration[5] are of obvious interest due to their similarity to *O*-methylhydroxylamine; they were also found to have rates of reaction within a detectable range. Since few studies on the rates of rapid, multistep reactions of silver(II) have been decribed, we are reporting on the reactions with NH_3OH^+ and $NH_3OCH_3^+$. (A more limited study of the reaction with $CH_3NH_2OH^+$ is included as it helps in elucidating the mechanisms.) The results afford a comparison with those obtained for manganese(III).[6]

Experimental Section

Reagents.—Preparation and standardization procedures for silver(I) perchlorate, sodium perchlorate (for maintaining ionic strength, μ), and perchloric acid were as described previously.[7] Solutions of hydroxylamine were made up immediately before use. Reagent grade hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) from Fisher was used without further purification. Excess silver(I) perchlorate was added to precipitate chloride, which was then removed by filtration. Solutions of *N*-methylhydroxylamine were prepared in a similar manner with *N*-methylhydroxylamine hydrochloride ($CH_3NHOH \cdot HCl$) from Aldrich.

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[1] The authors gratefully acknowledge partial support from Public Health Service Research Grant GM 08893-09 from the National Institute of General Medical Sciences, U. S. Public Health Service, and in part by National Science Foundation Grant GP 11529.

[2] G. Davies, K. Kustin, and L. J. Kirschenbaum, *Inorg. Chem.*, **7**, 146 (1968), reported the rate of reaction between Mn(III) and H_2O_2 but could not resolve the time course of the Ag(II) + H_2O_2 reaction; *cf.* H. N. Po, Ph.D. Thesis, University of California, Davis, Calif., 1967.

[3] Compare results in (a) G. Davies and K. Kustin, *Trans. Faraday Soc.*, **65**, 1630 (1969), with (b) D. H. Huchital, N. Sutin, and B. Warnqvist, *Inorg. Chem.*, **6**, 838 (1967).

[4] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, p 189.

[5] T. C. Bissot, R. W. Parry, and D. H. Campbell, *J. Amer. Chem. Soc.*, **79**, 796 (1957).

[6] G. Davies and K. Kustin, *Inorg. Chem.*, **8**, 484 (1969).

[7] (a) D. Honig and K. Kustin, *J. Inorg. Nucl. Chem.*, **32**, 1599 (1970). (b) No reduction of silver(I) by the hydroxylamines was observed to occur for several hours in these media, a period of time considerably longer than the actual experiment; *cf.*, C. P. Lloyd and W. F. Pickering, *ibid.*, **29**, 1907 (1967).

O-Methylhydroxylamine was obtained as the free base by distillation of the hydrochloride (K & K Laboratories) from 50% w/v aqueous NaOH. The distillate was collected up to 50°, distilled over NaOH pellets, then redistilled, and collected up to 48°. The base was stored at low temperatures under nitrogen. As the stock solutions are moderately unstable,[6] they were made up by weight immediately before use.

Silver(II) solutions were prepared by anodic oxidation.[8-10] The concentration of total Ag(II) was determined spectrophotometrically;[3b,7,8,11] absorbance readings were taken on a Beckman DU, using 1-cm silica cells. All readings were at 470 nm, where $\epsilon_{\mathrm{Ag(II)}}$ is 138 ± 2 M^{-1} cm^{-1}.[7]

Stoichiometry.—The concentrations of hydroxylamine and *O*-methylhydroxylamine and their products cannot be conveniently and accurately followed during and after reaction; only the change in silver(II) can be known accurately. Therefore, the stoichiometry will be given in the form of a silver(II) consumption ratio n, where n is defined as (moles of Ag(II) reacted)/(initial moles of substrate present). It will also be convenient, in the case of *O*-methylhydroxylamine, to define another ratio, namely, the ratio of total initial concentrations, $[\mathrm{Ag(II)}]_0/[\mathrm{NH_3OCH_3^+}]_0$, designated R.

The procedure for hydroxylamine and *O*-methylhydroxylamine with $R < 10$ is as follows, except where noted. Equal aliquots of a silver(II) solution were added to two volumetric flasks, one containing a known amount of substrate and the other similar in every respect but having no substrate. The amount of Ag(II) reacted would be equal to the difference in the two flasks.

When $R < 10$, all the silver(II) was consumed by *O*-methylhydroxylamine. The procedure at higher R ($R > 12$) was as follows. A silver(II) solution (3 ml) was placed into two 1-cm silica cells and the absorbance measured. To one of the cells, 10 μl of a known *O*-methylhydroxylamine solution was added, and the solution was stirred immediately. Absorbance readings were taken until the reaction was over. This procedure required several minutes. The amount of silver(II) that had reacted was determined by the difference in absorbance of the two cells.

A high-vacuum gas chromatography system was used to identify and measure any product gases in the reaction with *O*-methylhydroxylamine. Aliquots of Ag(II) and $\mathrm{NH_3OCH_3^+}$ were put into separate arms of a two-armed stoichiometry vessel. The solutions were degassed by ultrasonic agitation and freeze–thawing. The degassed solutions were then mixed, product gases, if any, being pumped off through a Dry Ice–acetone trap (∼−50°) into the calibrated volumes of a Toepler pump, where the pressure and volume of the gas were measured. The ambient temperature was also recorded at this time. The sample was then analyzed by gas chromatography.

Kinetics.—A stopped-flow apparatus was used for the kinetic determinations. For the reaction with *O*-methylhydroxylamine, the apparatus used (constructed of glass and quartz) has already been described.[12] A newly constructed apparatus was used to study the reaction with hydroxylamine and *N*-methylhydroxylamine.[13] This apparatus had a shorter dead time (∼2 msec) than the previous one (∼10 msec). This instrument was necessary for studying the reaction with hydroxylamine over an appreciable concentration range. However, it also had a small observation chamber, which resulted in a smaller signal-to-noise ratio. Consequently the error in the determination was somewhat greater at low [Ag(II)] for the new apparatus. The disappearance of silver(II) was followed spectrophotometrically at 470 nm, none of the other species present absorbing here. Freshly prepared solutions of silver(II) and substrate, of the same ionic strength and acidity, were mixed. The initial silver(II) concentration was determined by the average of absorbance readings of unreacted solution immediately before and after the stopped-flow run. The total time elapsed during a run was less than 10 min; the differences in absorbance readings were generally less than 5%. A stoichiometric excess of *O*-methylhydroxylamine was employed so that no silver(II) remained at the end of the reaction. Except for one run, the same procedure was followed with hydroxylamine. The reaction trace was recorded on a storage oscilloscope and photographed afterwards. Each run was repeated several times to ensure reproducibility. An example of a typical oscilloscopic trace is shown in Figure 1. All experiments were at 22 ± 1°.

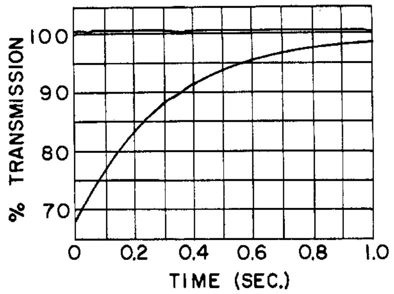

Figure 1.—Oscillograph of a stopped-flow experiment. The ordinate has been calibrated in percentage of light transmitted, the abscissa in seconds. (The horizontal trace corresponds to 100% transmission, obtained by triggering the oscilloscope electronically several seconds after the recording of the lower trace.) For this trace the experimental conditions are $[\mathrm{Ag(II)}]_0 = 1.35 \times 10^{-3}\ M$, $[\mathrm{NH_3OCH_3^+}]_0 = 3.29 \times 10^{-3}\ M$, $[\mathrm{Ag(I)}] = 3.76 \times 10^{-1}\ M$, $[\mathrm{HClO_4}] = 4.15\ M$, $\mu = 5.33\ M$, temperature 22 ± 1°, and path length 0.91 cm.

Results

In this section, we will first give the stoichiometric results and then the kinetic results. Of primary interest is a comparison among the rate constants. Since the reactions show a straightforward second-order rate law in terms of an apparent constant-acidity bimolecular rate constant, k_{app}, first-order in [Ag(II)] and in [substrate], a meaningful comparison can be made regardless of uncertainties in the stoichiometry. These ambiguities in stoichiometry arise for reactions in which immediate, intermediate, and final products cannot be completely identified. The results of product gas analysis are, however, in agreement with the determined stoichiometries insofar as they have been measured.

Stoichiometry. (A) Spectrophotometric Analysis. (a) Hydroxylamine.—The results in Table I show that, in the presence of excess Ag(II), the stoichiometric consumption ratio, n, is six. No attempt was made to measure nitrate produced, as the absorbance of silver(I) interferes with that of nitrate,[6] and the nitrate concentration is too low to permit detection of $\mathrm{AgNO_3^+}$.[7]

TABLE I

STOICHIOMETRY OF REACTION WITH HYDROXYLAMINE AT 22°: $[\mathrm{HClO_4}] = 2.45\ M$, $[\mathrm{Ag(I)}] = 0.163\ M$, AND $\mu = 2.61\ M^{a,b}$

$10^4[\mathrm{Ag(II)}]_0{}^c$	$10^4[\mathrm{Ag(II)}]_\infty{}^d$	$10^4[\mathrm{NH_3OH^+}]_0{}^c$	n^e
31.2	4.1	4.6	5.9
31.2	18.1	2.3	5.7
31.2	0	6.9	>4.5
23.0	6.4	2.77	6.0^f
24.6	6.8	2.99	6.0^f

[a] All concentrations are molar. [b] Determined by spectrophotometric analysis. [c] Subscript 0 refers to initial concentrations. [d] Subscript ∞ refers to final concentrations. [e] n = moles of Ag(II) consumed/mole of $\mathrm{NH_3OH^+}$. [f] Determined on stopped-flow apparatus.

(b) *O*-Methylhydroxylamine.—Attempts to measure n at low R ($R < 10$) were unsuccessful, as all the silver(II) was consumed (see Table II). At $R > 10$, n was measured, though the experimental error (∼10%)

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(8) G. Veith, E. Guthals, and A. Viste, *Inorg. Chem.*, **6**, 667 (1967).

(9) A. A. Noyes, D. Devault, C. D. Coryell, and T. S. Deahl, *J. Amer. Chem. Soc.*, **59**, 1326 (1937).

(10) A. A. Noyes and A. Kossiakoff, *ibid.*, **57**, 1238 (1935).

(11) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliffe, *J. Phys. Chem.*, **67**, 1617 (1963).

(12) L. J. Kirschenbaum, Ph.D. Thesis, Brandeis University, 1968.

(13) J. Martin and K. Kustin, unpublished results.

TABLE II

STOICHIOMETRY OF REACTION WITH *O*-METHYLHYDROXYLAMINE AT 22°[a,b]

$10^4[\text{Ag(II)}]_0$[c]	$10^4 \times [\text{Ag(II)}]_\infty$[c]	$10^4 \times [\text{NH}_3\text{OCH}_3^+]_0$[c]	*R*	*n*
22.7[d]	0	8.90	2.55	>2.55
20.1[e]	0	7.23	2.78	>2.79[f]
22.0[g]	0	4.40	5.00	>5.00
29.0[e]	0	3.08	9.42	>9.42[f]
Mol × 10⁶	Mol × 10⁶	Mol × 10⁶		
17.8[h]	3.90	1.11	16.0	12.5
15.5[h]	1.90	1.11	14.0	12.3
14.5[h]	0	1.11	13.0	≥13.0

[a] Unless otherwise noted, concentrations are molar. [b] Determined by spectrophotometric analysis. [c] Subscript 0 refers to initial concentrations (or amounts); subscript ∞ to final. [d] $[\text{HClO}_4] = 2.32$ *M*, $[\text{Ag(I)}] = 0.152$ *M*, $\mu = 2.47$ *M*. [e] $[\text{HClO}_4] = 4.78$ *M*, $[\text{Ag(I)}] = 3.76 \times 10^{-2}$ *M*, $\mu = 4.82$ *M*. [f] Determined on stopped-flow apparatus. [g] $[\text{HClO}_4] = 2.13$ *M*, $[\text{Ag(I)}] = 0.152$ *M*, $\mu = 2.28$ *M*. [h] $[\text{HClO}_4] = 4.8$ *M*, $[\text{Ag(I)}] = 3.76 \times 10^{-1}$ *M*, $\mu = 5.22$ *M*.

becomes significant; values of n were between 12 and 13. Complete oxidation of $NH_3OCH_3^+$ to CO_2 and NO_3^- would result in $n = 12$. For reasons mentioned above, no attempt was made to measure nitrate.

(B) Gas Analysis.—The results of an examination of the gaseous products from the oxidation of *O*-methylhydroxylamine are given in Table III. No gaseous products were observed at excess *O*-methylhydroxylamine. With excess silver(II), gaseous products were not detected at $R = 4.3$ but were detected at $R = 16$. The product was identified as CO_2; the yield, within experimental error, was consistent with $n = 12$. The fact that no N_2 was produced is consistent with the stoichiometry measured.

TABLE III

GASEOUS PRODUCTS FROM OXIDATION OF *O*-METHYLHYDROXYLAMINE[a]

Ag(II), mol[b]	$\text{NH}_3\text{OCH}_3^+$, mol[b]	*R*	Product gases, mol
3.47×10^{-5}	8.16×10^{-5}	0.425	No gaseous products detected
3.53×10^{-5}	3.61×10^{-4}	0.098	No gaseous products detected
2.74×10^{-5}	6.35×10^{-6}	4.31	No gaseous products detected
4.06×10^{-5}	2.55×10^{-6}	15.9	CO_2, 2.41×10^{-6}

[a] Apparatus could detect N_2, O_2, CO_2. [b] Initial amounts.

(C) Kinetic Analysis. (a) Hydroxylamine.—In the kinetic range, the reaction was found to be first order in each reactant. A value of $n = 6$, for stoichiometric excess of hydroxylamine, is consistent with the kinetic data in Table IV. The linearity of pseudo-first-order plots at low molar excess of hydroxylamine, the linearity of second-order plots with silver(II) in stoichiometric excess, and the similarity of k_{app} with silver(II) in stoichiometric excess are consistent with this stoichiometry. Assuming values of $n < 6$ gives both greater spread in k_{app} and deviations from linearity. In the analogous reaction of Mn(III), complete oxidation of NH_3OH^+ to NO_3^- was observed when hydroxylamine was present in stoichiometric excess.[6] As silver(II) is both a stronger oxidizing agent and is generally kinetically more reactive, a similar result is expected.

TABLE IV

KINETIC DATA FOR REACTION WITH HYDROXYLAMINE AT 22°[a]

$[\text{HClO}_4]$	$10[\text{Ag(I)}]$[b]	$10^4[\text{Ag(II)}]_0$[c]	$10^4 \times [\text{NH}_3\text{OH}^+]_0$[c]	$10^{-5}k_\text{A}$[d]
		$\mu = 2.61$		
2.45	1.63	24.6[e]	2.99	1.40
	1.63	19.6	5.05	1.16
	1.63	17.2	5.04	1.79
	0.82[f]	16.1	5.04	1.88
	1.63	8.77	5.05	1.44
	1.63	6.27	15.9	1.01[g]
	1.63	6.05	1.59	0.99
	1.63	1.90	9.90	0.71[g,h]
	1.63	1.74	0.99	0.75[h]
				Av 1.24 ± 0.5 × 10⁵ M^{-1} sec⁻¹
		$\mu = 3.35$		
2.45	4.41	12.1	4.75	1.52
	0.326	10.4	4.75	1.86
		$\mu = 5.95$		
1.03	1.15	8.08	4.23	3.33
1.99	1.15	8.95	3.58	1.90
2.95	1.15	9.60	3.73	1.43
3.91	1.15	9.75	3.73	1.03
4.87	1.15	10.6	3.58	0.807
5.83	1.15	10.3	4.23	0.756

[a] All concentrations are molar. [b] Total silver concentration as Ag(I). [c] Subscript 0 indicates initial concentrations. [d] Units are M^{-1} sec⁻¹. [e] Stoichiometric excess of Ag(II). [f] Ionic strength = 2.53 *M*. [g] From pseudo-first-order plots. [h] Considerable error due to low [Ag(II)].

TABLE V

KINETIC DATA FOR REACTION WITH *O*-METHYLHYDROXYLAMINE AT 22°[a]

$[\text{HClO}_4]$	$10^2[\text{Ag(I)}]$[b]	$10^4[\text{Ag(II)}]_0$[c]	$10^4 \times [\text{NH}_3\text{OCH}_3^+]_0$[c]	$10^{-3}k_\text{A}$[d]
		$\mu = 2.42$		
2.38	3.76	4.31	28.4	9.0[e]
		10.7	59.2	9.9
		11.6	39.6	10.4
		6.84	14.5	10.4
		17.0	28.9	12.8
		4.53	5.65	13.5
				Av 11.0 ± 2.5 × 10³ M^{-1} sec⁻¹
		$\mu = 5.33$		
1.79	3.76	9.18	15.0	5.11
		7.59	30.3	4.35
2.38		8.00	34.5	3.27
		9.78	33.8	3.41
2.97		12.7	22.6	2.08
		6.01	133	1.86[f]
3.56		6.23	35.7	1.97
		6.05	17.0	2.04
4.15		14.1	34.4	1.52
		5.76	33.3	1.28
	37.6	14.8	34.0	1.13
	37.6	13.5	32.9	1.17
5.29	3.76	10.2	36.1	1.07
		8.33	19.1	1.07

[a] All concentrations are molar. [b] Total silver concentration as Ag(I). [c] Subscript 0 indicates initial concentrations. [d] Units are M^{-1} sec⁻¹. [e] Similar value from pseudo-first-order plot. [f] From pseudo-first-order plot.

(b) *O*-Methylhydroxylamine.—At $R < 1$, the reaction was found to be first order in each reactant, and the kinetic data were only consistent with the assumption of the stoichiometry being $n = 2$. At $R = 0.472$ and 0.802, a pseudo-first-order plot gives significant deviations from linearity, indicating $n < \sim 5$. At

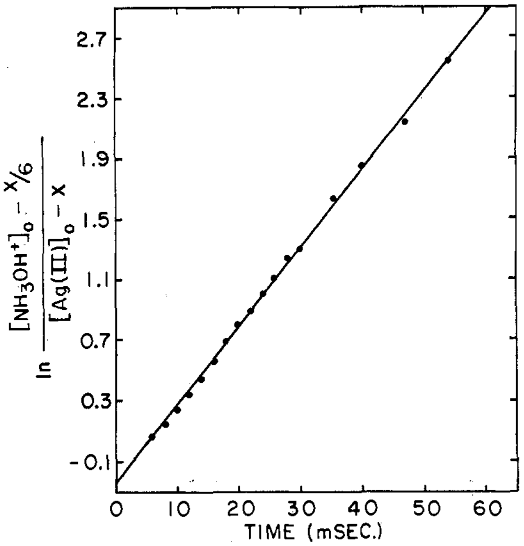

Figure 2.—Typical second-order plot for reaction with hydroxylamine. Experimental conditions are $[HClO_4] = 2.45\ M$, $\mu = 2.61\ M$, $[Ag(I)] = 0.163\ M$, $[Ag(II)]_0 = 8.77 \times 10^{-4}\ M$, $[NH_3OH^+]_0 = 5.05 \times 10^{-4}\ M$, and temperature 22 ± 1°.

$R = 0.802$ assuming a value of 1 or 3 for n gives significant deviations from linearity, while assuming $n = 2$ gives a linear plot. As R decreased, deviations from linearity at $n \neq 2$ became progressively smaller, as would be expected. The range in "second-order" rate constants for different values of R (and different initial reactant concentrations) at constant $[HClO_4]$, $[Ag(I)]$, and μ is within experimental error for $n = 2$ (see Table V), but is far greater for $n = 1$.

Kinetics. (a) **Hydroxylamine.**—The results are given in Table IV. For reasons already mentioned, the experimental error may be $\geq 20\%$ at low $[Ag(II)]$. The experimentally observed rate is given by[14]

$$-\frac{d[Ag(II)]}{dt} = k_{app}[Ag(II)][NH_3OH^+] \tag{1}$$

The integrated form of the rate law is[14]

$$\ln \frac{[NH_3OH^+]_0 - x/6}{[Ag(II)]_0 - x} = \left([NH_3OH^+]_0 - \frac{[Ag(II)]_0}{6}\right)k_{app}t + \ln \frac{[NH_3OH^+]_0}{[Ag(II)]_0} \tag{2}$$

where $x \equiv$ concentration of silver(II) consumed. The left-hand side of eq 2 is plotted against time, with the slope of the resulting straight line being equal to $k_{app}([NH_3OH^+]_0 - [Ag(II)]_0/6)$. A typical plot is shown in Figure 2. At $\mu = 2.16\ M$, $[HClO_4] = 2.45\ M$, and $[Ag(I)] = 0.163\ M$, k_{app} seemed to increase somewhat as $[Ag(II)]_0$ increased, but the trend was not consistent. As both pseudo-first-order and fully integrated plots were linear, contribution from a pathway involving silver(II) to an order greater than one must be within experimental error. The trend is most likely due to experimental error, with the possibility of a small contribution from a higher order reaction. Therefore, experiments designed to observe possible variations in rate with $[Ag(I)]$ and $[HClO_4]$ were carried out under conditions where $[Ag(II)]_0$ would not be too different. In addition, other concentrations were also kept as constant as possible. The rate was found to be independent of $[Ag(I)]$, as the results of experiments at $\mu = 3.35\ M$ and $[HClO_4] = 2.45\ M$ show. Comparison of results at different ionic strengths and the same $[HClO_4]$ show a very slight increase in k_{app} with increasing ionic strength (the value of k_{app} at $\mu = 5.95\ M$ and $[HClO_4] = 2.45\ M$ was estimated as being between the values at higher and lower acidities). The results at $\mu = 5.95\ M$ show an appreciable decrease in k_{app} with increasing $[HClO_4]$.

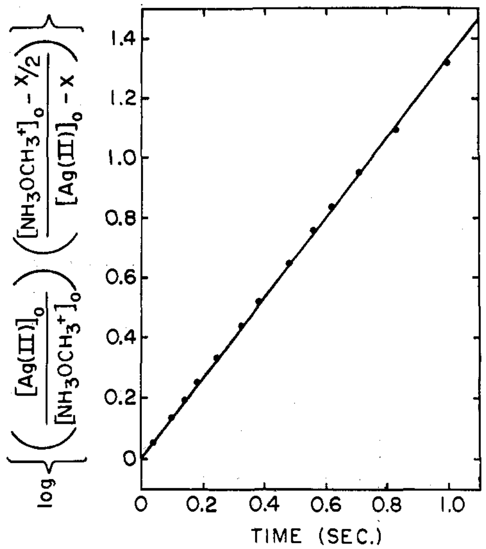

Figure 3.—Typical second-order plot for reaction with *O*-methylhydroxylamine, with $n = 2$. Experimental conditions are the same as for Figure 1. The per cent transmittance is converted to optical density, so that the parameter x could be calculated.

(b) ***O*-Methylhydroxylamine.**—A quantitative analysis was carried out for $R < 1$; the results are given in Table V. The experimental error is $\sim\pm 20\%$. As mentioned, linearity of graphical plots was only obtained by assuming $n = 2$, where the rate was first order in each reactant. The experimentally observed rate is given by

$$-\frac{d[Ag(II)]}{dt} = k_{app}[Ag(II)][NH_3OCH_3^+] \tag{3}$$

The integrated form of the rate law is

$$\ln \frac{[NH_3OCH_3^+]_0 - x/2}{[Ag(II)]_0 - x} = \left([NH_3OCH_3^+]_0 - \frac{[Ag(II)]_0}{2}\right)k_{app}t + \ln \frac{[NH_3OCH_3^+]_0}{[Ag(II)]_0} \tag{4}$$

where x is as defined in eq 2. The rate constant, k_{app}, is obtained by a procedure analogous to that for hydroxylamine. A typical plot is shown in Figure 3. Results at $\mu = 5.33\ M$ and $[HClO_4] = 4.15\ M$ indicate the rate is independent of $[Ag(I)]$. As is the case with hydroxylamine, k_{app} decreases as $[HClO_4]$ increases. There is also a significant decrease in k_{app} when the ionic strength is increased (compare results at $[HClO_4] = 2.38\ M$).

The stoichiometry of $n = 2$ at $R < 1$, found from

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[14] Strictly speaking, the stoichiometric consumption ratio should appear in the rate law, *i.e.*, rate $\equiv -(1/n)\, d[Ag(II)]/dt$. However, as we are interested in the first step of the reactions studied, the rate will be given with respect to Ag(II): S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 18.

kinetic analysis, implies that the disappearance of an amount of silver(II) corresponding to twice the amount of initial *O*-methylhydroxylamine present is considerably more rapid than the disappearance of the remaining silver(II). That is, with an overall stoichiometry of $n = 12$ and the disappearance of each of the 12 Ag(II) per $NH_3OCH_3^+$ corresponding to a "stoichiometric step," the first two stoichiometric steps are considerably more rapid than the remaining ones at $R < 1$. The stoichiometry experiments on the Beckman DU verified that the final few steps are considerably slower than the initial ones, the reaction taking minutes for completion.

Stopped-flow runs were also done at $R > 1$. With $R = 9.42$, the first two steps were essentially complete; only the subsequent steps could be observed. At the end of the slowest observable time period, 50 sec, the reaction was not yet complete. Another run at $R = 2.79$, however, indicated that the first two stoichiometric steps, while more rapid, were not that much more rapid than the third step under the experimental conditions (see Table II). Therefore, the kinetic data for $R < 1$ are only consistent with a stoichiometry of $n = 2$; at higher R, the reaction will become more complex.

(c) ***N*-Methylhydroxylamine.**—Stopped-flow experiments were carried out with $CH_3NH_2OH^+$ to help elucidate the mechanisms of the other substrate reactions. At $\mu = 2.56\ M$, $[HClO_4] = 2.40\ M$, $[Ag(I)] = 0.163\ M$, $[Ag(II)]_0 = 4.22 \times 10^{-4}\ M$, and $[CH_3NH_2OH^+]_0 = 1.73 \times 10^{-3}\ M$, $k_{app} \simeq (1.6 \pm 0.6) \times 10^5\ M^{-1}\ sec^{-1}$. The value of k_{app} was obtained from a pseudo-first-order plot (which was linear). The reaction was over in 25–30 msec. Under similar conditions and reactant concentrations, the same result was obtained with NH_3OH^+, while with $NH_3OCH_3^+$ the reaction took ~300–350 msec. In addition, k_{app} was essentially identical with that for NH_3OH^+, while it is approximately an order of magnitude greater than that for $NH_3OCH_3^+$. Interestingly, the reaction with NH_4^+, under the same conditions, was much slower than with $NH_3OCH_3^+$; however, the extent of this reaction is uncertain.

Mechanism

The reactions of NH_3OH^+ and $NH_3OCH_3^+$ both show a significant acid dependence. At the high acidities necessary for Ag(II), both hydroxylamine and *O*-methylhydroxylamine are present as NH_3OH^+ and $NH_3OCH_3^+$, respectively, since the acid dissociation constants for both substrates are of the magnitude $K_a \sim 10^{-6}\ M$ ($K_a = [H^+][base]/[acid]$).[6] Rate constants for neutral substrate pathways would have to exceed the diffusional limit ($\gtrsim 10^9\ M^{-1}\ sec^{-1}$) to contribute. (This assumption may be somewhat in error for $NH_3OCH_3^+$, the slowest reacting substrate.) Previous studies have indicated the presence of $AgOH^+$ in significant amounts at the high acidities used.[7] Values for K_H, where $K_H = [AgOH^+][H^+]/[Ag^{2+}]$, varied from ~0.1 to 0.7 M at $\mu = 5.6\ M$. Acid–base equilibria of the type involved with Ag^{2+}–$AgOH^+$ are generally very rapidly established.[15]

Therefore, the acid dependence can be treated by

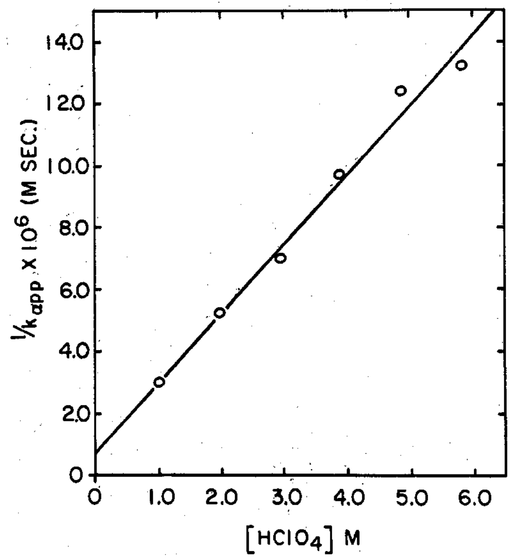

Figure 4.—Plot of $1/k_{app}$ *vs.* $[H^+]$ for reaction with hydroxylamine at $\mu = 5.95\ M$ and 22°.

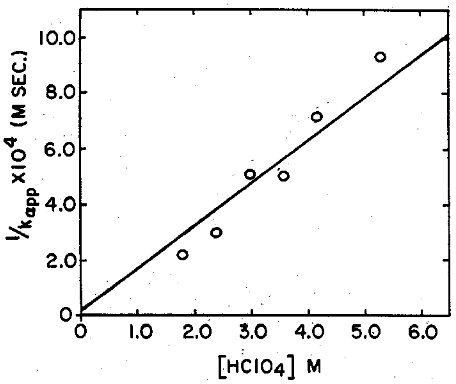

Figure 5.—Plot of $1/k_{app}$ *vs.* $[H^+]$ for reaction with *O*-methylhydroxylamine at $\mu = 5.33\ M$ and 22°.

assuming that it is due to differences in the reactivity of Ag^{2+} and $AgOH^+$ with the substrates. The apparent second-order rate constant for the disappearance of total silver, $[Ag(II)] = [Ag^{2+}] + [AgOH^+]$, is related to the rate constants for reactions of the two free silver species by

$$k_{app}[Ag(II)] = k[Ag^{2+}] + k'[AgOH^+] \qquad (5)$$

Under the assumption that the protolytic steps are always equilibrated, this expression can be rewritten as

$$k_{app}\{[H^+] + K_H\} = k[H^+] + k'K_H \qquad (6)$$

Initial treatment of the data according to eq 6 indicated that $k[H^+] \ll k'K_H$ for both these substrates. This condition simplifies eq 6, which then becomes

$$1/k_{app} = [H^+]/k'K_H + 1/k' \qquad (7)$$

Consequently, plots of $1/k_{app}$ should be linear; the slope is $1/k'K_H$ and the intercept is $1/k'$. This plot is shown for NH_3OH^+ in Figure 4 and for $NH_3OCH_3^+$ in Figure 5. With NH_3OH^+, the plot is linear; a value of $K_H = 0.32 \pm 0.14\ M$ is obtained. The rate constants are given in Table VI. With $NH_3OCH_3^+$, there is uncertainty as to the applicability of eq 7. It is quite possible that the acid dependence is greater than eq 7 indicates (see also Figure 6 in ref

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[15] (a) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. React. Kinet.*, **2**, 287 (1964); (b) P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, **75**, 929 (1971).

TABLE VI

RATE CONSTANTS FOR REACTIONS OF Ag^{2+} AND $AgOH^+$ AT 22°[a]

		M^{-1} sec^{-1}	
Substrate	μ, M	Ag^{2+}	$AgOH^+$
$NH_3OCH_3^+$	5.33	$<10^3$	$\simeq(2 \pm 1) \times 10^4$
NH_3OH^+	5.95[b]	$<10^4$	$(1.4 \pm 0.5) \times 10^6$
$CH_3NH_2OH^+$	2.56		$k_{app} \simeq (1.6 \pm 0.6) \times 10^5$

[a] Assuming $K_H = 0.32 \pm 0.14$ M. [b] As this reaction showed very little dependence on μ, the results can be compared with those for $NH_3OCH_3^+$ at $\mu = 5.33$ M.

6). A plot of log k_{app} *vs.* log $[HClO_4]$ gives an inverse power of 1.4 for $[HClO_4]$. However, the data can be *approximately* fit to eq 7, as Figure 5 shows. The value of K_H found in the analysis of the NH_3OH^+ data was thus used to determine k' and an upper limit of k for reaction of Ag(II) with $NH_3OCH_3^+$.

(A) **Hydroxylamine.**—A mechanism (eq 8–10), identical with that proposed for the reaction with Mn(III),[6] can be applied to the disappearance of silver(II) in the reaction with hydroxylamine to obtain the empirical rate law (eq 1 and 2). Reactions 8 and 9 represent single-step processes.

$$Ag^{2+} + NH_3OH^+ \xrightarrow{k} Ag^+ + NH_2O\cdot + 2H^+ \tag{8}$$

$$AgOH^+ + NH_3OH^+ \xrightarrow{k'} Ag^+ + NH_2O\cdot + H_3O^+ \tag{9}$$

$$2H_2O + 5Ag(II) + NH_2O\cdot \xrightarrow{k_1} 5Ag^+ + NO_3^- + 6H^+ \tag{10}$$

$$k_1 \gg k,\ k'$$

Evidence that the radical produced in (8) and (9) derives from loss of the hydroxyl and not the amine hydrogen may be found by considering the *O*-methylhydroxylamine results. Namely, if, in the first step, both compounds lost their amine hydrogens, no appreciable difference in rate would be expected. Similar rates are clearly not observed, for the NH_3OH^+ reaction is more than an order of magnitude more rapid than is the $NH_3OCH_3^+$ reaction.

Furthermore, secondary generation of the $NH_2O\cdot$ radical is also precluded. That is, a sequence compatible with the stoichiometry, but involving $\cdot NHOH$ as the primary product, such as

$$Ag^{2+} + NH_3OH^+ \longrightarrow Ag^+ + \cdot NHOH + 2H^+$$

$$HONH\cdot + HONH_3^+ \longrightarrow HONH_2 + NH_2O\cdot + H^+$$

$$H^+ + HONH_2 \rightleftarrows NH_3OH^+$$

would also be ruled out.

(B) ***O*-Methylhydroxylamine.**—At $R < 1$, the following general mechanism is consistent with the empirical rate law (eq 3 and 4).

$$Ag^{2+} + NH_3OCH_3^+ \xrightarrow{k} Ag^+ + \cdot NHOCH_3 + 2H^+ \tag{11}$$

$$AgOH^+ + NH_3OCH_3^+ \xrightarrow{k'} Ag^+ + \cdot NHOCH_3 + H_3O^+ \tag{12}$$

$$\cdot NHOCH_3 + Ag(II) \xrightarrow{k_2} Ag^+ + Prod \tag{13}$$

$$nH_2O + Prod + 10Ag(II) \xrightarrow{k_3} NO_3^- + CO_2 + 10Ag^+ + yH^+ \tag{14}$$

$$k_2 \gg k,\ k' > k_3$$

Reactions 11–13 represent single-step processes.

The identities of the products in the initial steps 11–13 are unclear. A comparison with the hydroxylamine results shows definitely that, initially, $NH_2O\cdot$ + $\cdot CH_3$ cannot be products, as then the stoichiometry in the kinetic region ($R < 1$) should be $n \geq 6$, and not $n = 2$ as observed. Abstraction of a hydrogen attached to carbon is generally slower, leaving $\cdot NHOCH_3$ as the most likely product (see Discussion).

Discussion

The results indicate that for the initial step in the oxidation of $NH_3OCH_3^+$ and NH_3OH^+ by Ag(II), $AgOH^+$ is considerably more reactive than Ag^{2+}. A step involving H atom transfer would be more favorable for $AgOH^+$ than for Ag^{2+}; however, both Ag(II) species may be reacting by direct electron transfer. Whether or not the reactions proceed by an inner-sphere or outer-sphere mechanism exclusively is also uncertain, as water exchange on Ag(II) would be expected to be considerably more rapid than the processes measured here.[16] In the oxidation of acetic and formic acids by silver(II), an acid-dependent rate could also be ascribed to differences in reactivity of $AgOH^+$ and Ag^{2+}.[13]

As was the case with Mn(III),[6] Ag(II) oxidizes NH_3OH^+ to NO_3^-. It is likely that a free-radical mechanism is involved for these reactions. With Ce(IV) as the oxidant, the stoichiometry was dependent on both acidity and R ($R \equiv [\text{oxidant}]_0/[NH_3OH^+]_0$); the rates of reaction were much lower than those with Mn(III) and Ag(II).[17] Waters and Wilson suggest $NH_2O\cdot$ as the initial product. Depending on R, dimerization of $NH_2O\cdot$ to give N_2 or further reaction with Ce(IV) takes place.[17a] The proposed reaction of $NH_2O\cdot$ with Mn(III) or Ag(II) is extremely rapid. The initial step in the reaction of NH_3OH^+, formation of $NH_2O\cdot$, is more than an order of magnitude more rapid with Ag(II) than with Mn(III).

A recent pulse-radiolysis study has shown that NH_2OH is oxidized by OH radical to give $\cdot NHOH$ as the first product.[18] However, as mentioned, the evidence presented here for Ag(II) does not support this conclusion for reaction with hydroxylamine. The same situation occurs for the Mn(III) study.[6] With respect to *O*-methylhydroxylamine, however, the initial reaction may very well be H atom abstraction from the nitrogen. This step will be considered more fully below.

The oxidation of $NH_3OCH_3^+$ by Ag(II) is both more rapid and extensive than oxidation by Mn(III).[6] In the case of Mn(III), the stoichiometry was observed to be a function of R, n (where $n = \Delta[Mn(III)]/[NH_3OCH_3^+]_0$) approaching 1 as R approached 1 and being between 2 and 3 with $R \gtrsim 5$. A complete "leveling off" in the stoichiometry was not observed; that is, as R increased so did n, though at $R \gtrsim 5$, the increase was slight. At $R < 1$, the kinetics were consistent with a value of $n = 1$. These observations indicate that with $R < 1$, the first step in the reaction is considerably more rapid than the subsequent steps; as R increases, the second and third steps become observable. The final steps, if they occur, are much too slow to be observed in the time needed for the stoichi-

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[16] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 145–158, remarks on d^9 systems therein.

[17] (a) W. A. Waters and I. R. Wilson, *J. Chem. Soc. A*, 534 (1966); (b) N. Hlasivcová, J. Novák, and J. Zýka, *Collect. Czech. Chem. Commun.*, **32**, 4403 (1967); (c) *ibid.*, **32**, 4410 (1967).

[18] M. Simic and E. Hayon, *J. Amer. Chem. Soc.*, **93**, 5982 (1971).

ometry measurements. At excess $NH_3OCH_3^+$ and excess Mn(III), no gaseous products were observed.

In the case of Ag(II), the first step is slower than the second, but it is considerably more rapid than the subsequent steps at $R < 1$. As R increases, the subsequent steps are complete within minutes. The oxidation of acetic and formic acids by silver(II) produces CO_2, with the initial step being rate determining.[13] The observed rate constants are almost three orders of magnitude less than k_{app} for the Ag(II)–$NH_3OCH_3^+$ system; the time scale for the reactions of acetic and formic acids is comparable to that for the complete oxidation of $NH_3OCH_3^+$.

The fact that the subsequent steps are much more rapid with Ag(II) than Mn(III) is not surprising, as k_{app} for Ag(II) is roughly three orders of magnitude greater than for Mn(III). The fact that, with Ag(II), the second step is much more rapid than the first at $R < 1$ is surprising. In the reaction with Mn(III), the radical $\cdot NHOCH_3$ was postulated as the first product (this species is consistent with the already mentioned pulse radiolysis study[18]); at $R < 1$, its dimerization was assumed to be much more rapid than its reaction with Mn(III). If $\cdot NHOCH_3$ is also the initial product in the reaction with Ag(II), further reaction of Ag(II) with $\cdot NHOCH_3$ or the postulated dimer, $N_2H_2(OCH_3)_2$, is extremely rapid. Since the dimer is probably relatively unreactive, it is likely that the Ag(II) + $\cdot NHOCH_3$ reaction competes favorably with the radical–radical dimerization itself. This difference in reactivity between Mn(III) and Ag(II) may be compared to the previously mentioned difference in the reactivity of Ce(IV) and Mn(III) with NH_3OH^+. For Ag(II), as for Mn(III), but not for Ce(IV), no gaseous products were observed.

The possibility of pathways involving Ag(III) being significant can be ruled out for both substrates. If Ag(III) were involved appreciably, a second-order dependence on [Ag(II)] and an inverse first-order dependence on [Ag(I)] would be expected.[11,19,20] The strong dependence of k_{app} on μ in the reaction of $NH_3OCH_3^+$ is interesting relative to the apparent insensitivity to this parameter in the reaction of NH_3OH^+. The source of this variation is unknown. The differences in reactivity of $NH_3OCH_3^+$ compared with other substrates with Mn(III) were also suggested as possibly being due to difficulties in coordination and H bonding of $NH_3OCH_3^+$ to Mn(III). The same may be the case with Ag(II), though at lower ionic strength the difference is not that great.

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[19] H. N. Po, J. H. Swinehart, and T. L. Allen, *Inorg. Chem.*, **7**, 244 (1968).

[20] See J. Pumies, W. Roebke, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **72**, 844 (1968), and B. M. Gordon and A. C. Wahl, *J. Amer. Chem. Soc.*, **80**, 273 (1958), for the rate of 2Ag(II) → Ag(III) + Ag(I).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHEASTERN UNIVERSITY, BOSTON, MASSACHUSETTS 02115

Xenon(II) Difluorophosphates. Preparation, Properties, and Evidence for the Difluorophosphate Free Radical

BY MAX EISENBERG AND DARRYL D. DESMARTEAU*

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Xenon(II) fluoride difluorophosphate, $FXeOPOF_2$, and xenon(II) bis(difluorophosphate), $Xe(OPOF_2)_2$, are obtained in high yield by reactions of xenon difluoride with μ-oxo-bis(phosphoryl difluoride), $P_2O_3F_4$, at 22° in trichlorofluoromethane. The new compounds are pale yellow solids which decompose readily at 22° forming an unstable material, which is probably the difluorophosphate free radical.

Introduction

Several new xenon compounds have recently been prepared by reactions of the xenon fluorides with strong oxy acids.[1–5] Xenon fluorosulfates, perchlorates, trifluoroacetates, pentafluorotellurates, and possibly nitrates have been obtained by this method. All of these compounds have been obtained with XeF_2 and both the mono- and bis-substituted derivatives have been prepared. No xenon(IV) and one xenon(VI) fluorosulfate have been synthesized to date from XeF_4 and XeF_6.

Attempts to extend this method of preparation to the synthesis of xenon(II) difluorophosphates using difluorophosphoric acid have been unsuccessful, because of side reactions involving fluorination of phosphorus. We have now obtained both $FXeOPOF_2$ and $Xe(OPOF_2)_2$ by the reaction of XeF_2 with pure $P_2O_3F_4$ in CCl_3F. The compounds have only limited stability at 22° similar to the isoelectronic xenon(II) fluorosulfates, but unlike the lattter they do not yield a stable peroxide on decomposition.

Experimental Section

General Data.—Manipulations of volatile compounds were carried out in a Monel–Kel-F vacuum system or a glass system equipped with glass–Teflon valves. Pressures were measured with a Barton 316SS bellows gauge in the metal system and a mercury manometer in the glass system. Kel-F No. 3 polymer oil was used to protect the mercury. Amounts of volatile materials were determined by *PVT* measurements or by weight. Xenon and oxygen were identified by their physical properties

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* To whom correspondence should be addressed at the Department of Chemistry, Kansas State University, Manhattan, Kansas 66502.

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[3] F. Sladky, *Angew. Chem.*, **81**, 536 (1969).

[4] F. Sladky, *ibid.*, **81**, 330 (1969).

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